Effect of Polymer Surface Modification on Polymer–Protein Interaction via Hydrophilic Polymer Grafting

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ABSTRACT: Surface modification of flat sheet ultrafiltration membranes, polyethersulfone (PES), was investigated to improve the hydrophilicity of the membrane surface thereby reducing adsorption of the proteins onto the membrane. Grafting of hydrophilic polymers onto UV/ozone-treated PES was used to improve the hydrophilicity of the commercial PES membranes. Hydrophilic polymers, that is, poly(vinyl alcohol) (PVA), polyethylene glycol (PEG), and chitosan, were employed to graft onto PES membrane surfaces because of their excellent hydrophilic property. The surfaces of modified PES membranes were characterized by contact angle measurement, FTIR, and AFM. The FTIR spectra indicated that PES membranes were successfully modified by grafting of the hydrophilic polymers. The modified PES membranes showed 20% to 50% reduction in contact angle measurements in comparison with those of the virgin PES membrane. The tapping mode AFM technique was employed to investigate the changes of surface topography, cross-section, and root mean square roughness of the modified PES membrane surfaces. The modified PES membranes showed elevated roughness (ranging from 7.0 to 25.7 nm) compared with that of the virgin PES membrane (2.1 nm). It is concluded that grafting of PVA, PEG, or chitosan onto UV/ozone-treated PES membranes increases hydrophilicity and lowers protein adsorption by 20% to 60% compared to the virgin PES membrane. Among the 3 hydrophilic polymers studied, PEG showed the most favorable result in terms of contact angle and protein adsorption.

Keywords: AFM, FTIR, membrane fouling, polymer grafting, protein adsorption, UV/ozone treatment

Introduction

Many researchers have demonstrated that an increase in hydrophilicity of membranes significantly reduced membrane fouling as a result of the reduced hydrophobic interaction between proteins and membrane surfaces (Musale and Kulkarni 1996; Hester and others 1999). In membrane separations involving protein solutions, the "ideal" membranes are hydrophilic membranes that minimize protein adsorption (and consequently minimal fouling). Unfortunately, most commercial membranes used in ultrafiltration of proteins are relatively hydrophobic due to their superior properties to hydrophilic membranes in mechanical, thermal, and chemical stability.

The extent of protein adsorption on membranes depends on the various types of interactions between protein molecules and the membrane surface, such as van der Waals interaction, electrostatic interactions, hydrophobic interaction, dipole–dipole interaction, and hydrogen bonding (Hamza and others 1997). One of the main factors enhancing the protein adsorption onto polymeric membranes is hydrophobic interaction. Therefore, protein adsorption on the polymeric membrane can be reduced by modifying the hydrophobic membrane surface so it is more hydrophilic. These modified membranes are easier to clean because the adsorbed protein molecules can be easily removed from the more hydrophilic surface due to weak protein-membrane bonding (Kim and others 2002).

Surface modification of polymeric membranes also plays a positive role in membrane performances such as permeation flux, lifespan, and selectivity. Surface modification of polymeric membranes results in the formation of 2 distinct polymer layers. The thin surface layer governs the selectivity, flux, and adsorption of solute while the thick substrate layer provides the mechanical strength and chemical stability. The incorporation of hydrophilic polymer through blending (Rajagopalan and others 2004; Wang and others 2006b), coating (Wei and others 2005), and surface grafting (Ulbricht and Riedel 1998; Song and others 2000; Kim and others 2002) has been developed to improve the protein adsorption resistance and permeation property of polymeric membranes. Among various techniques employed to improve the hydrophilicity of the PES membrane surface, hydrophilic polymer grafting involving UV/ozone treatment is one of the easiest, fast, and low-cost ways to modify the polymeric membrane surfaces. This technique has been shown to be successful in increasing the surface hydrophilicity and permeability and decreasing the membrane fouling during the protein filtration (Thom and others 1998; Kilduff and others 2000; Pieracci and others 2002).

In this study, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), and chitosan were used as hydrophilic polymers for grafting owing to their excellent hydrophilicity. Poly(vinyl alcohol) has been well known for its excellent film-forming property, emulsifying property, and minimal cell and protein adhesion property

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(Peppas and Wright 1996; Shukla and others 2005). Poly(ethylene glycol) has extraordinary antifouling property to protein adsorption due to its hydrophilicity, flexible long chains, large exclusion volume, and unique coordination with surrounding water molecules in an aqueous solution (Wang and others 2006a). Chitosan is a linear polyelectrolyte carrying positive charges and has been identified as a nontoxic, biodegradable, biocompatible, and hydrophilic polysaccharide. Chitosan-based membranes have been used for protein separations (Zeng and Ruckenstein 1998).

Materials and Methods

Materials

The flat sheet ultrafiltration membrane, polyethersulfone (PES) (YMPWSP3001), was purchased from Sterlitech Corp. (Kent, Wash., U.S.A.). MWCO (molecular weight cut-off) of flat sheet PES membrane was 20000. Polyethylene glycol (PEG) 2000 and poly(vinyl alcohol) (PVA) (MW 146000 to 186000) were purchased from Sigma-Aldrich (St. Louis, Mo., U.S.A.). Chitosan (MW 300000, DOD 90%) was purchased from Kunpoong Bio Co., Ltd. (Jeju, South Korea). UV/ozone cleaner, which was used to activate the PES membrane surface for grafting of the hydrophilic polymers on the membrane surface, was purchased from Jelight Co. (Irvine, Calif., U.S.A.).

Grafting polymerization using UV/ozone

UV/ozone treatment was carried out to initiate and activate the PES membrane surface for grafting with hydrophilic polymers. The dried small piece of PES flat membrane was exposed to UV/ozone treatment for 1 to 30 min. Peroxide groups were formed on the activated membrane surface by ozone treatment. The peroxide groups generated on the membrane surface reacted with hydrophilic polymers, that is, PVA, PEG 2000, and chitosan. Twenty percent (w/v) PVA, 20% (w/v) PEG 2000, and 1% (w/v) chitosan solutions were used to react with the activated PES membranes (Table 1). The basic forming mechanism of peroxide groups after UV/ozone treatment on the PES surface has been described in the literature (Nyström and Järvinen 1991). The grafting reaction was performed in a glass ampoule at 70 °C for 2 h. After the grafting reaction with hydrophilic polymers, the PES membranes were rinsed with distilled water for 24 h to remove excess hydrophilic polymers from the PES membrane surface. The hydrophilic polymer grafted PES membranes were subsequently dried at room temperature under vacuum.

Contact angle measurement

The contact angles of the unmodified and modified PES membranes were measured by the sessile drop method on a VCA Optima surface analysis system (AST Products Inc., Billerica, Mass., U.S.A.). A 28 gauge blunt-tip needle attached to a mechanically controlled micrometer of VCA Optima was used to dispense a 2 μL deionized water droplet onto the surface of membrane samples. Five measurements were made for each sample and used to determine the average and standard deviation.

Table 1—PES membrane samples and methods used for the surface modification.

Sample nr	Modification method
1	Virgin PES membrane
2	UV/ozone for 20 min and 20% PVA grafting
3	UV/ozone for 20 min and 20% PEG 2000 grafting
4	UV/ozone for 20 min and 1% chitosan grafting

ATR-FTIR spectra

ATR-FTIR spectra of unmodified and modified PES membranes were measured using a Thermal Nicolet Nexus 670 FTIR system with an ATR accessory. The ATR accessory containing a ZnSe crystal (25 × 5 × 2 mm) with a nominal incident angle of 45° yielded about 12 internal reflections at the sample surface. All spectra were recorded with 256 scans at 4.0 cm^{-1} resolution at room temperature.

Atomic force microscopy (AFM)

The surface topography and cross-sectional roughness of modified PES membranes were characterized by using tapping mode AFM (Multimode SPM, Nanoscope IIIa, Digital Instruments, Woodburg, N.Y., U.S.A.) with a silicon probe. Several specimens were scanned in order to obtain their morphologies.

Protein adsorption on modified PES membranes

Static adsorption of β-lactoglobulin on the modified PES membrane surface was compared using UV-Vis spectrophotometer via the absorbance at 280 nm with the amount of the protein adsorbed by the virgin PES membrane. For this study, the concentration of β-lactoglobulin of 2.5 mg/mL and solution pH of 3.0 were chosen because the maximum adsorption was observed under this condition in the previous report (Kim and others 2007).

Results and Discussion

Characterization of virgin PES membrane using ATR-FTIR

In the commercial polymeric membrane manufacture process, preservatives have commonly been used to stabilize membranes to protect the membranes from microbial attack, and to extend their shelf life. As shown in Figure 1A, preservatives induced a very strong band at 3313 cm^{-1} and 3 bands at 1647, 1037, and 923 cm^{-1}, which are the same spectra of the preservatives in a previously reported research (Belfer and others 2000). Preservatives were washed out with deionized (DI) water and dried at room temperature for several days for the characterization of the native PES membrane. All PES membranes used for surface modification were washed with DI water for 24 h to remove preservatives and dried at room temperature (about 25 °C). The spectra of the washed PES membrane have no strong band at 3400 cm^{-1}, which indicates the aliphatic C–H stretching but 2 small bands associated with aromatic C–H vibration are present at 3095 and 3069 cm^{-1} as shown in Figure 1B. There is no band at around 3500 to 3600 cm^{-1} which is associated with the O–H stretching vibration of water molecules, so this IR spectrum supports that PES membrane was dried completely after washing out the membrane preservatives.

Grafting polymerization using UV/ozone

Prior to grafting of the polymers onto the membranes, PES membrane was treated with UV/ozone to activate its surfaces. To optimize the UV/ozone treatment time, contact angle was measured in 48 h after UV/ozone treatment from 0 to 30 min. The contact angle of the virgin PES membrane was about 71 degrees but it was decreased greatly after UV/ozone treatment. As shown in Figure 2, the contact angle of PES membrane treated with UV/ozone decreases with treatment time, plateauing after 20 min. The contact angle of the PES membrane was decreased greatly within 5 min of UV/ozone treatment and was followed by slow decrease with UV/ozone treatment time. The contact angle of the PES membrane

treated with UV/ozone for 20 min was almost half that of the virgin PES membrane.

Physical modifications such as plasma, radiation, and ion beams treatments have a major drawback: the surface reactivity can be gradually deteriorated over time. To investigate the surface recovery of UV/ozone-treated PES membrane over time, the contact angle of PES membrane exposed to UV/Zone for 20 min (which is observed as the optimum treatment time) was monitored for 48 h (Figure 3). The contact angle of the PES membrane exposed to UV/ozone for 20 min was increased back from 11 to 38 degrees in 48 h. Since the contact angle of the original PES membrane was 71 degrees, it corresponds to about 50% recovery after 48 h. The rate of the recovery decreased over time. Most recovery occurred in 5 h after UV/ozone treatment. After 48 h, the contact angle reached plateau. Based on this result, all surface characterization was conducted 48 h after UV/ozone treatment.

Although the PES membrane treated with UV/ozone was stored in the air, the surface property such as contact angle was not changed significantly after 48 h; the contact angle of the PES membrane increased up to 60 degrees if the UV/ozone-treated PES membrane was exposed to aqueous environment. Therefore, UV/ozone treatment alone is not sufficient to improve PES hydrophicility; grafting of hydrophilic polymer had to be performed to prevent recovery of the surface properties of the PES membrane in solutions. For that reason, hydrophilic polymers such as PVA, PEG, and chitosan were grafted onto PES membranes after UV/ozone treatment for 20 min. The chemical reaction schemes are illustrated in Figure 4.

Concentration effect of hydrophilic polymers

Figure 5 shows the FTIR spectra of poly(vinyl alcohol) grafted PES membrane. Poly(vinyl alcohol) has exhibited a broad band from 3600 to 3650 cm^{-1}, which may be attributed to stretching hydroxyl (-OH) group of free alcohol, a broad band from 2850 to 3000 cm^{-1} that may be attributed to stretching alkyl C–H groups, and from 3200 to 3570 cm^{-1} for hydrogen bonds (Peppas and

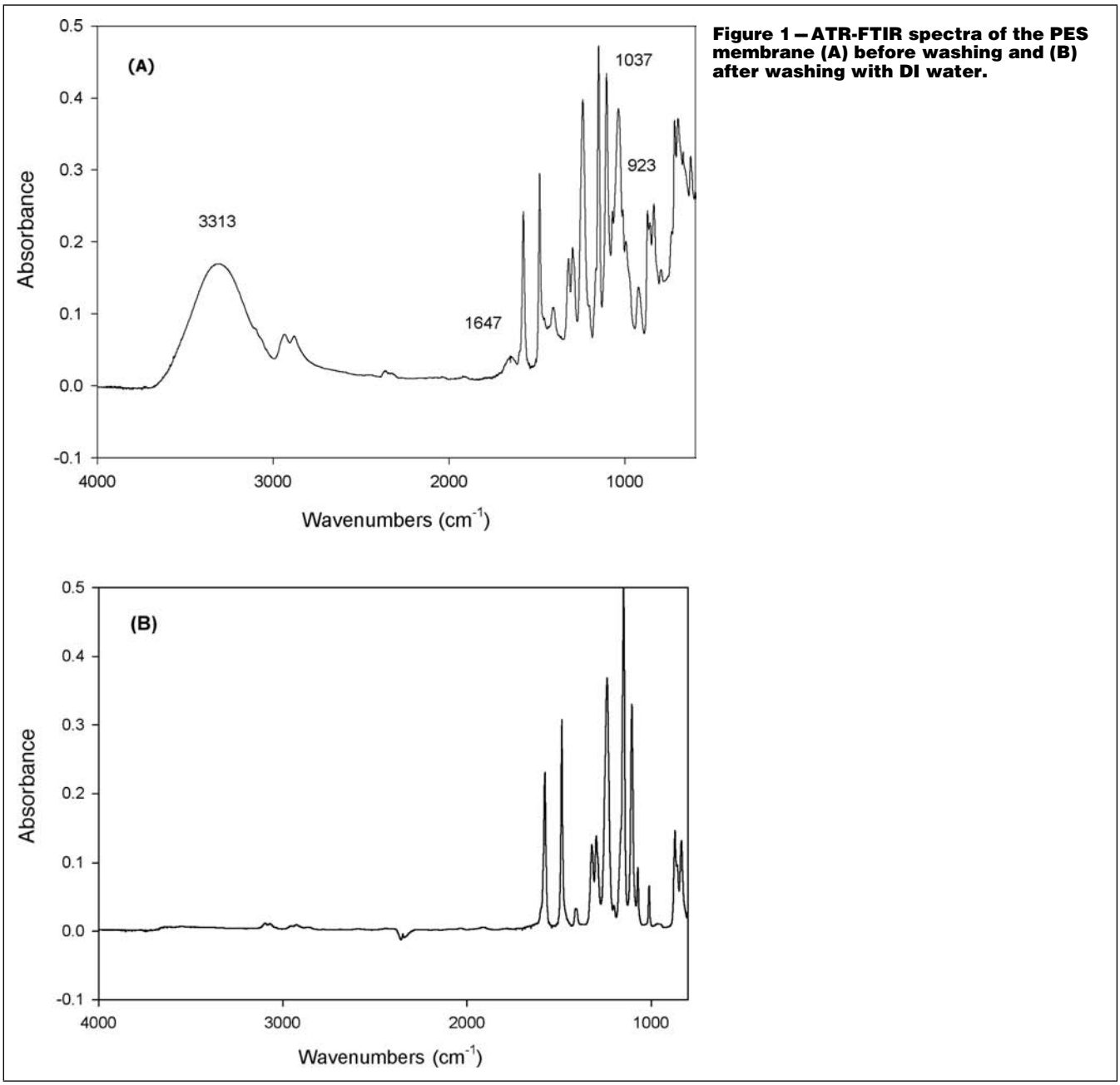

Figure 1 — ATR-FTIR spectra of the PES membrane (A) before washing and (B) after washing with DI water.

Wright 1996; Mansur and others 2004). The PVA-grafted PES membrane has exhibited a broad band at 3312 and at 2939 cm^{-1}, which are assigned to stretching hydroxyl (-OH) group of free alcohol and stretching alkyl C–H group of PVA, respectively. The intensities of these bands at 3312 and at 2939 cm^{-1} were increased with PVA concentration. These observations suggest that PVA polymer molecules are effectively grafted onto the PES membrane surface.

Figure 6 shows the FTIR spectra of PEG-grafted PES membrane. The molecular structure ($HO\text{-}CH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_n\text{-}CH_2\text{-}OH$) of PEG has exhibited strong absorption bands from 1050 to 1150 cm^{-1} for the stretching of ether groups, from 2850 to 3000 cm^{-1} for stretching alkyl (CH_2) groups, and from 3200 to 3600 cm^{-1} for hydroxyl (-OH) group from FTIR spectroscopy measurements (Mansur and others 2004). The major characteristic bands of PEG-grafted membrane showed some new or intensity increased peaks at 961.7 and at 2875 cm^{-1}, which were ascribed to C–H rock and C–C stretch, and C–H symmetric stretch of PEG, respectively. These observations showed that the PEG chains were successfully grafted onto the surface of the UV/ozone-treated PES membrane.

The difference in FTIR spectra between chitosan-grafted membranes and the virgin PES membrane was unobservable as indicated in Figure 7. We believe that the concentration (1% to 3% for chitosan compared with 20% for PEG and PVA) of chitosan solution used in the grafting reaction was too low to show a distinct difference in the spectra. As shown in Figure 5 and 6, the low concentration of PVA or PEG did not generate a clear difference in the spectra between the virgin PES and modified PES either. However, due to the higher molecular weight of chitosan, preparations of chitosan solutions for grafting reactions beyond 3% are impractical because of the extremely high viscosity of chitosan solutions.

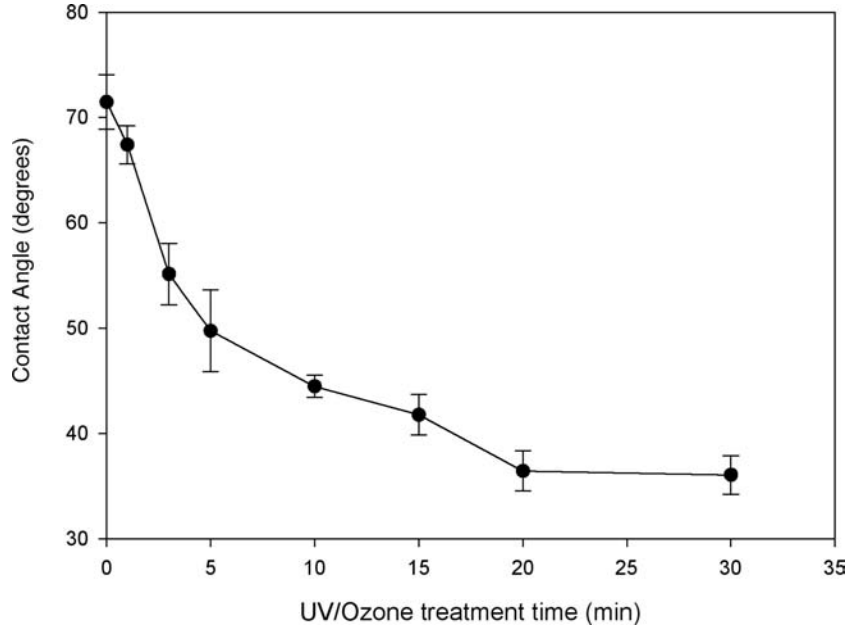

Figure 2—UV/ozone treatment effect on the contact angle of PES membranes.

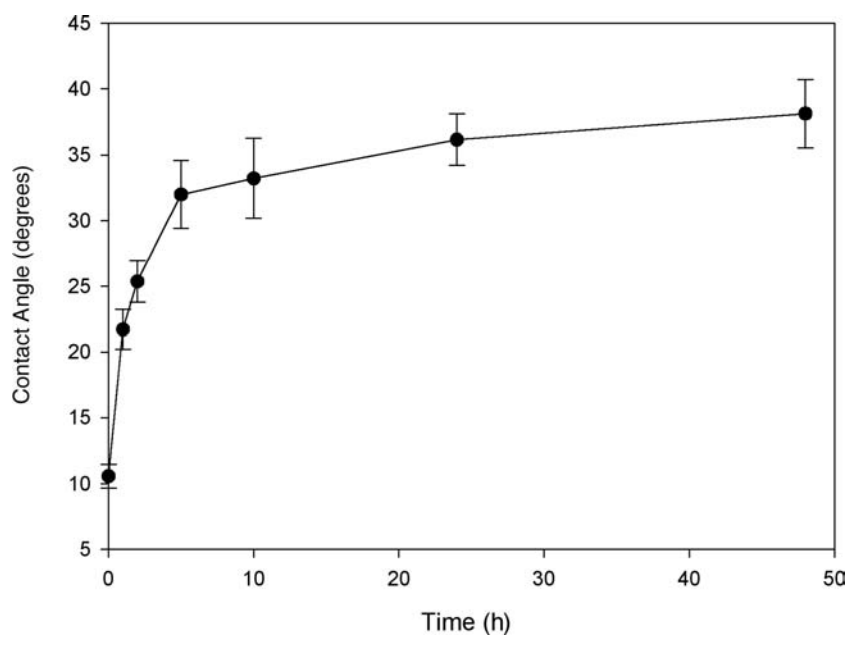

Figure 3—Contact angle recoveries of UV/ozone-treated PES membrane over time.

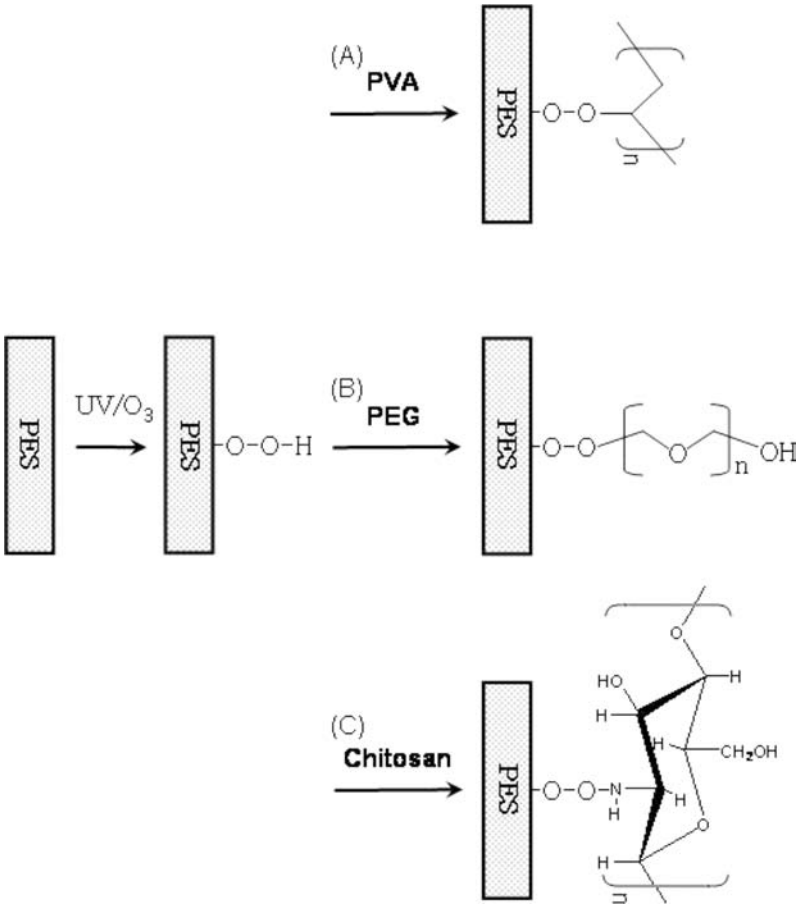

Figure 4—Reaction schemes of the hydrophilic polymers grafting onto the PES membrane activated by UV/ozone treatment: (A) PVA, (B) PEG, and (C) chitosan.

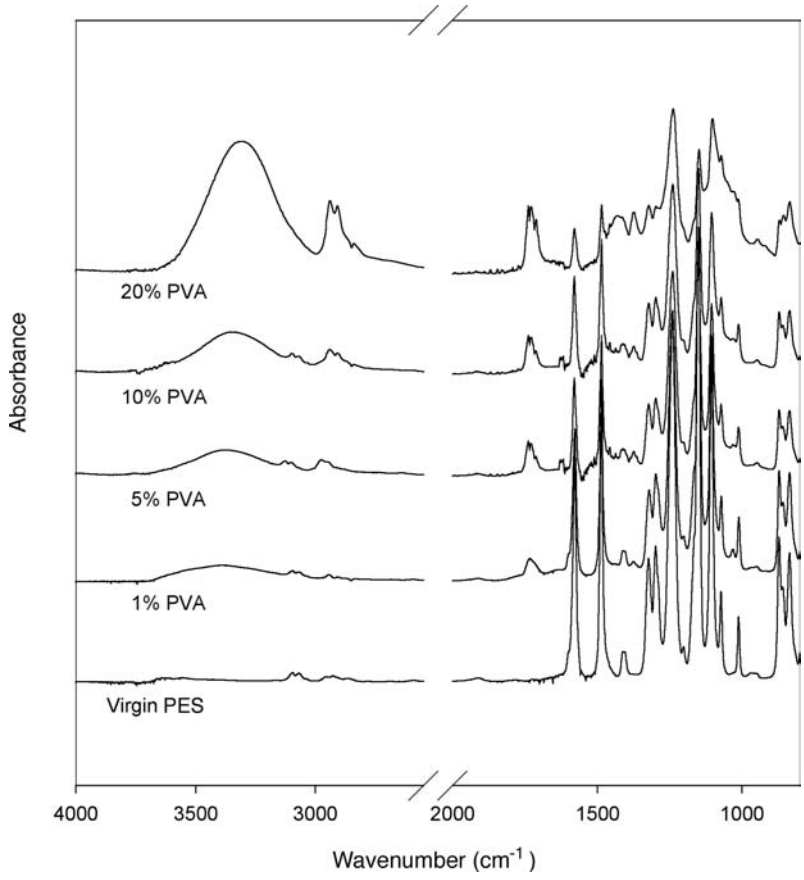

Figure 5—ATR-FTIR spectra of PVA-grafted PES membrane using UV/ozone treatment. The concentration of PVA ranged 1%, 5%, 10%, and 20%.

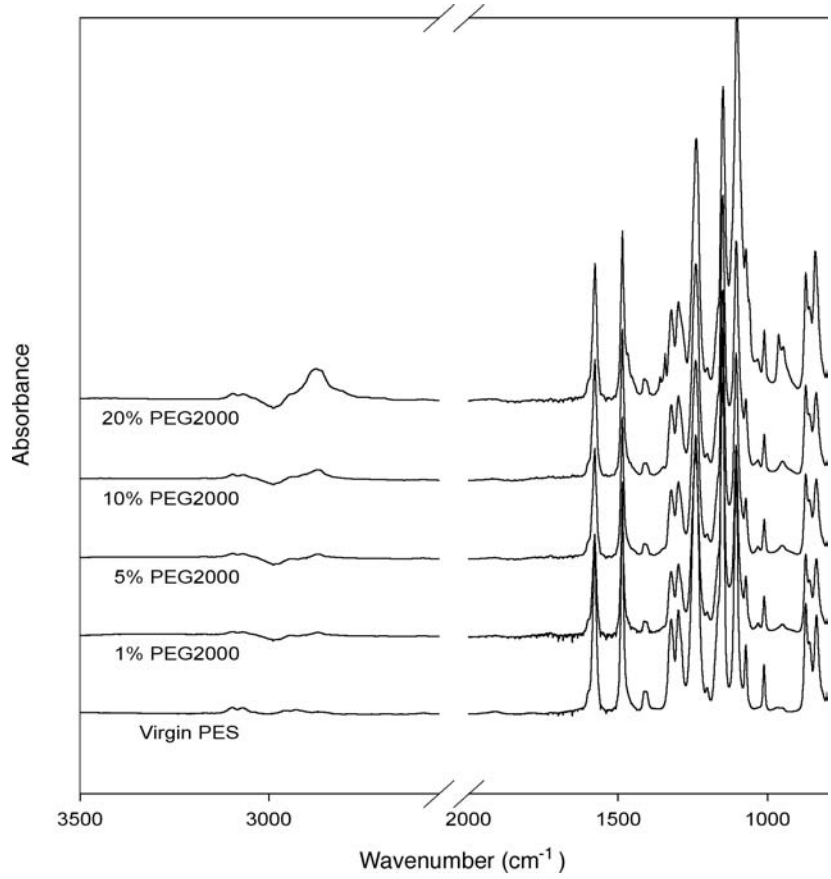

Figure 6—ATR-FTIR spectra of PEG 2000 grafted PES membrane using UV/ozone treatment. The concentration of PEG 2000 ranged 1%, 5%, 10%, and 20%.

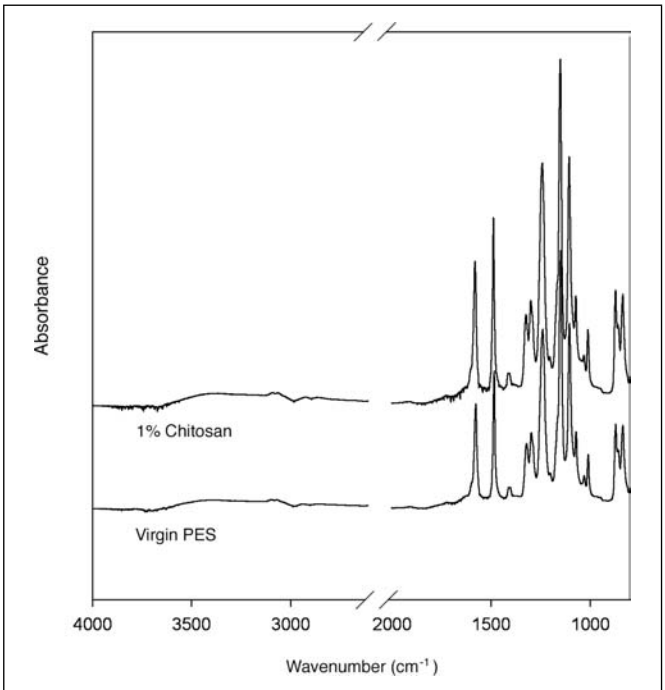

Figure 7—ATR-FTIR spectra of chitosan-grafted PES membrane using UV/ozone treatment. The concentration of chitosan was 1%.

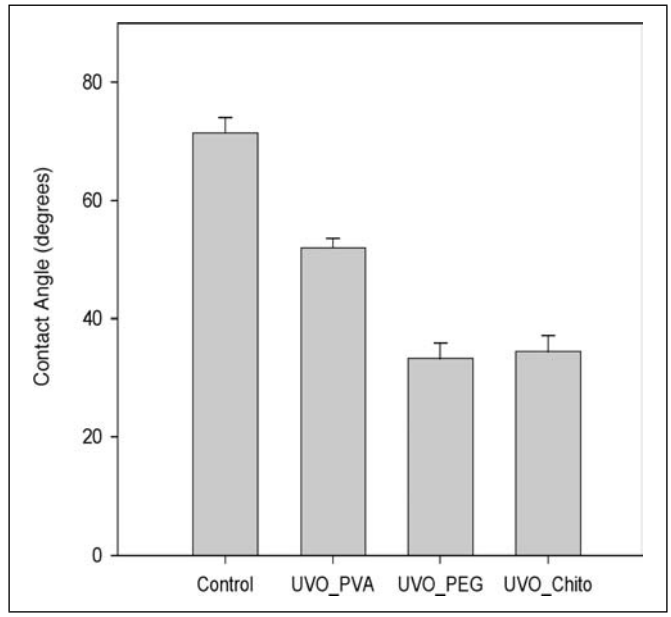

Figure 8—Contact angle of modified PES membranes.

Contact angle of the modified PES membranes

Contact angles of the modified PES membranes were measured and compared with that of the virgin PES membrane. As shown in Figure 8, contact angles of PES membranes were reduced by 20% to 50% after the surface modification. UV/ozone treatment could reduce the contact angle of PES membrane to about 36 degrees (as shown in Figure 2) but the contact angle could be recovered to about 60 degrees when UV/ozone-treated PES was immersed in the aqueous environment such as DI water. When the PES membrane was grafted with hydrophilic polymers, that is, PVA,

PEG, and chitosan after UV/ozone treatment, however, the contact angles of the modified PES membranes were lower than 60 degrees. This confirms that hydrophilic polymers were successfully grafted onto the PES membrane. Contact angles of modified PES membranes were varied with the type of hydrophilic polymers. PVA-modified membranes by UV/ozone showed contact angles of about 52 degrees. PEG- and chitosan-grafted PES membranes showed contact angles of about 35 and 36 degrees, respectively. Lower contact angle means that the modified membrane was changed to a more hydrophilic surface and it is expected to lower protein adsorption because of the reduced hydrophobic interaction. Based on the contact angle data, these modified PES membranes were expected to show much lower protein adsorption than the virgin PES membrane.

Atomic force microscopy (AFM)

Figure 9 represents AFM surface images of virgin PES (Figure 9A) and all modified PES membranes (Figure 9B, 9C, and 9D) with a projection area of 2 × 2 μm, in which the unique and characteristic ridge-and-valley structure of the PES membranes is clearly shown. The root mean square roughness for virgin PES, PVA-grafted PES, PEG-grafted PES, and chitosan-grafted PES are 2.0, 7.0, 25.7, and

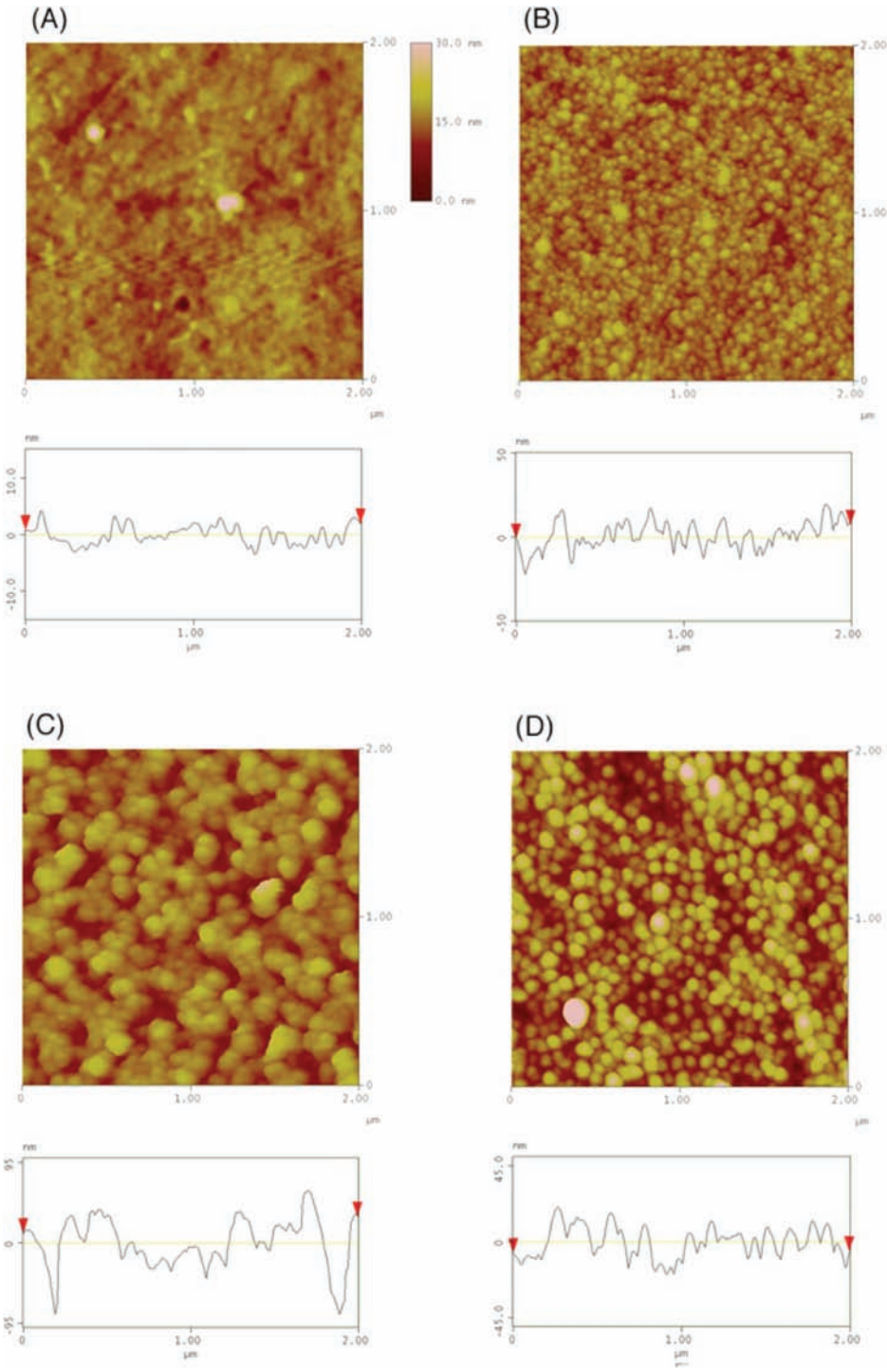

Figure 9—Tapping mode AFM images of topography and cross-sectional roughness: (A) virgin PES membrane (nr 1), (B) PVA-grafted PES membrane (nr 2), (C) PEG-grafted PES membrane (nr 3), and (D) chitosan-grafted PES membrane (nr 4). The root mean square roughness is (A) 2.1 nm, (B) 7.0 nm, (C) 25.7 nm, and (D) 10.1 nm. Image size is 2 × 2 μm.

10.1 nm, respectively. The bar between Figure 9A and 9B indicates the variations of the elevations in the membrane surface, the bright region indicates the highest level, and the dark region indicates the lowest level. The surface of the virgin PES membrane is rough. However, the surfaces of the modified PES membranes by hydrophilic polymer grafting are even rougher than that of the virgin PES membrane. These AFM images clearly show the variations in the morphology of the PES membrane before and after the polymer grafting.

Protein adsorption on modified membranes

Static adsorption of β-lactoglobulin on the modified PES membrane surface was studied to compare the decrease in the amount of adsorption on the modified PES membranes. As shown in Figure 10, the amount of β-lactoglobulin adsorbed on the PES membrane was reduced by 20% to 60% by the membrane surface modification. Among the modified PES membranes, the PEG-grafted PES membrane showed the lowest protein adsorption. Because the PEG-grafted membrane showed the lowest contact angle, the low hydrophobic interaction between protein and modified PES membrane was already expected. However, chitosan-grafted PES membrane showed the highest protein adsorption in modified PES membranes although the contact angle of this membrane showed the lowest value. But it still showed a lower protein adsorption than the virgin PES membrane. Although it could reduce the hydrophobic interaction between protein and modified membrane, it is speculated that chitosan-grafted membrane could increase the electrostatic interaction between free amine groups in chitosan and carboxyl and/or hydroxyl groups in the protein. In this scenario, the protein adsorption would increase in the chitosan-grafted membrane. Therefore it is expected that the protein adsorption on chitosan-grafted membrane would be increased more if more chitosan molecules were grafted onto the PES membrane.

Conclusions

In this study, we demonstrated a novel and effective method for the hydrophilic surface modification of PES membranes by grafting hydrophilic polymer using UV/ozone. This was aimed at reducing protein adsorption on polymeric ultrafiltration/nanofiltration membranes such as PES. PVA, PEG, and chitosan were chosen as hydrophilic polymers to be grafted onto PES membranes because of their excellent hydrophilic property. Surface properties of the modified PES membranes were characterized by contact angle, FTIR, and AFM. The instrument measurements indicated the extent of hydrophilic modification of the PES membrane with various hydrophilic polymers. The static adsorption experiment was also used to validate the effectiveness of the hydrophilic grafting onto PES membranes by comparing the result to that of unmodified PES membrane. The experimental results show that modified membranes have more hydrophilic surface and could reduce the amount of protein adsorption by 20% to 60%. This outcome shows that modification of PES membranes by hydrophilic polymer grafting is an effective technique to improve the hydrophilicity of PES membranes. This study has demonstrated that PEG showed the most favorable result in modifying PES membrane for fouling reduction among the 3 hydrophilic polymers examined. Present method would be useful for the development of less-susceptible-to-fouling membranes for ultrafiltration of proteins.

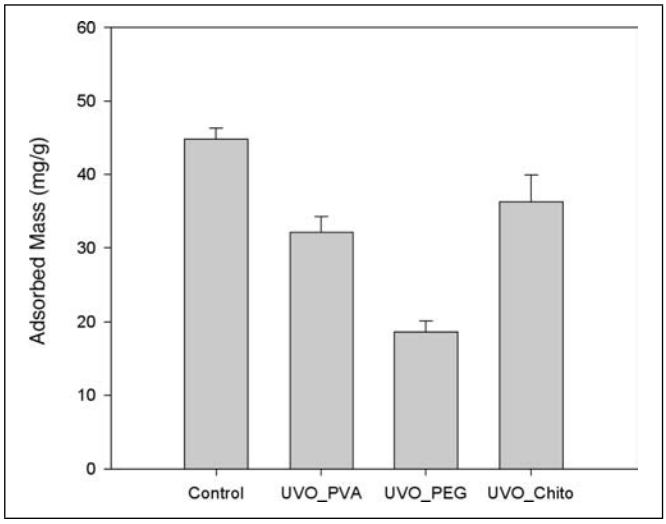

Figure 10—Mass of the β-lactoglobulin adsorbed on the unmodified and modified PES membranes by static adsorption experiment. The concentration of β-lactoglobulin was 2.5 mg/mL and the solution pH was 3.0.

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